ISSN: 0975 -8542

Journal of Global Pharma Technology

Available Online at: www.jgpt.co.in

RESEARCH ARTICLE

Optical Nonlinearity of Thiazine Dyes Doped With Nanoparticles of Liquid Crystals

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Abstract

The optical nonlinearity of several thiazine dyes such as(azure A and azure B) organic dyes doped with nanoparticles of liquid crystals in ethanol solvent has been studied using diode pump solid state laser at wavelength(457 nm) and power (56 mW) as the source of excitation. The optical responses were characterized by measuring the intensity dependent refractive index (n_2) of the medium using the Z-Scan technique. The results indicate that the samples of organic dyes doped with nanoparticles of liquid crystals possess very large linear and nonlinear optical properties as compared with samples of pure organic dyes. This result showed that these organic doped dyes are very suitable for applications in optical devices and can be available for applications as active laser medium.

Keywords: *Organic laser dyes, Z-Scan technique, Nonlinear optical properties, Liquid crystals.*

Introduction

Nonlinear optical properties have been the subject of numerous investigations theoretically and experimentally during recent years due to their applications to many branches. The nonlinear optical properties are important parameters in characterizing and determining the applicability of any material to nonlinear optical device [1]. Liquid crystals exhibit large photo induced nonlinearity due to their large dielectric anisotropy coupled with the collective director reorientation, it has a wide variety of products, from large industrial displays to a wide array of consumer electronics in homes and offices[2].

Organic materials exhibiting nonlinear absorption are currently of interest because of their large third-order nonlinearities, instantaneous response time, ease of processing, structural modifications and their applicability over a wide range of wavelengths[3].Laser dyes are promising compounds for nonlinear optical applications because they exhibit strong nonlinear-optical behavior[4].

Thiazine dyes are suitable for the study of photo-sensitized reactions in micellar media, because of their low ionization potential caused by the presence of two hetero-atoms [5]. Azure A and azure B is an organic dyefrom thiazine dyeshaving good photo-thermal stability, dissolvability and easy preparation virtue and also found to have noticeable third order nonlinearity [6].In this paper, we characterize the nonlinear response of (Azure A and Azure B) organic dyesdoped with nanoparticles of liquid crystalsin ethanol solvent. The nonlinear characterization was performed with the Z-Scan technique using diode pump solid state laser at (457 nm) and power (56 mW).

Theory

There is considerable interest in finding materials having fast nonlinearities. This interest, that is driven primarily by the search for materials for all-optical switching and sensor protection applications, concerns both nonlinear absorption (NLA) and nonlinear refraction (NLR). The absorption of the material at high intensity is given by [7]:

$$\alpha = \alpha_o + \beta I \ldots\ldots\ldots\ldots\ldots \ldots\ldots(1)$$

Where Iis the incident intensity, $\alpha_o$is the linear absorption coefficient and β is the

nonlinear absorption coefficient related to the intensity. At high intensity, the refractive index is given by [7]:

$$n = n_o + n_2 I \ldots\ldots\ldots\ldots\ldots(2)$$

Where n_o is the linear refractive coefficient and $n_2$is the nonlinear refractive coefficient.

The nonlinear optical properties can be investigated by Z-Scan technique at which it can be used to determine the nonlinear refractive index when closed-aperture geometry is used, and nonlinear absorption coefficient with open aperture. The nonlinear refractive index is calculated from the peak to valley difference of the normalized transmittance by the following formula [8]:

$$n_2 = \frac{\Delta\Phi_o}{I_o L_{eff} K} \ldots\ldots\ldots\ldots\ldots(3)$$

Where $\Delta\ \Phi_o$ is the nonlinear phase shift:

$$\Delta T_{p-v} = 0.406|\Delta\Phi_o| \ldots\ldots\ldots\ldots(4)$$

ΔT_{p-v} the difference between the normalized peak and valley transmittances, $k = 2\pi/\lambda$, λ is the beam wavelength, I_o is the intensity at the focal spot and L_{eff} is the effective length of the sample, determined from [9] :

$$L_{eff} = \frac{(1 - exp^{-\alpha_o L})}{\alpha_o} \ldots\ldots\ldots(5)$$

Where L is the sample length andα_o is linear absorption coefficient which is given as [9]

$$\alpha_o = \frac{\ln(\frac{1}{T})}{t} \ldots\ldots\ldots\ldots\ldots(6)$$

Where (t) is the thickness of sample and T is the transmittance.

The linear refractive index (n_o) obtained from equation [10]:

$$n_o = \frac{1}{T} + \left[\left(\frac{1}{T^2} - 1\right)\right]^{1/2} \ldots\ldots\ldots(7)$$

The intensity at the focal spot is given by [10]

$$I_o = \frac{2P_{peak}}{\pi {\omega_o}^2} \ldots\ldots\ldots\ldots\ldots(8)$$

Is defined as the peak intensity within the sample at the focus, where ω_o is the beam radius at the focal point.The coefficients of nonlinear absorption (*β*), can be easily calculated by using following equation [10]:

$$\beta = \frac{2\sqrt{2}\ T(z)}{I_o L_{eff}} \ldots\ldots\ldots\ldots(9)$$

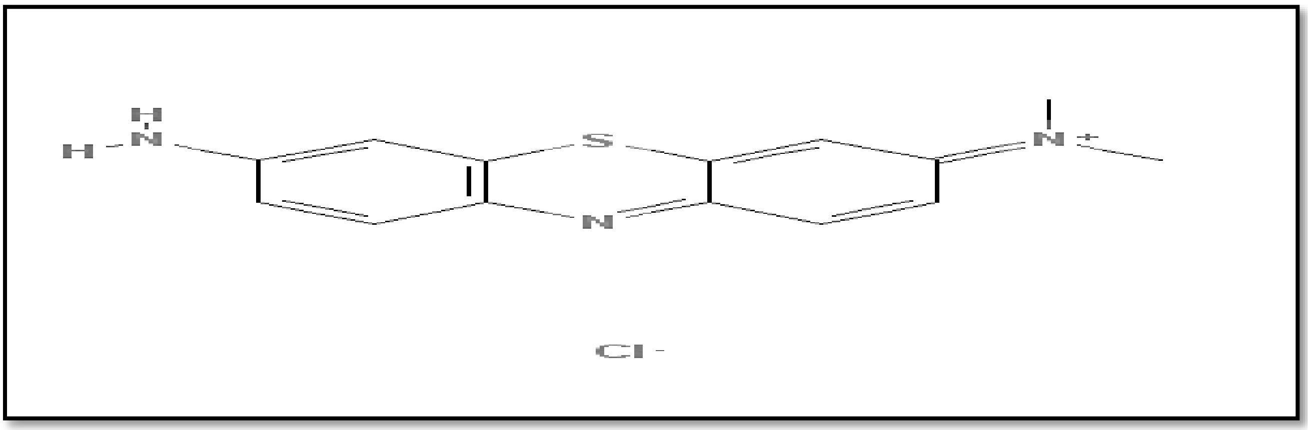
Where T (z): The minimum value of normalized transmittance at the focal point, where (Z=0)

Materials and Methods

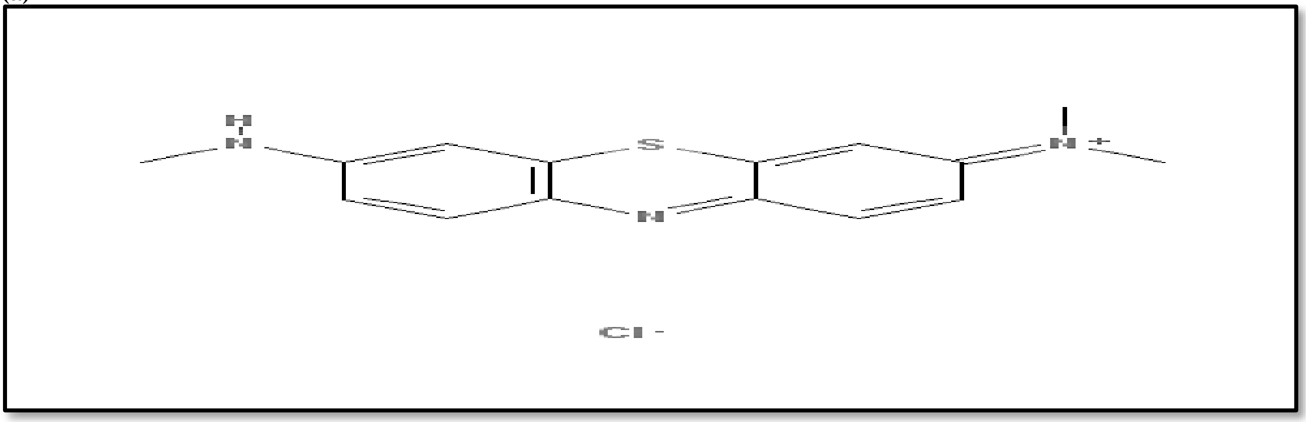
The liquid crystal used (Di-Cinnamylidene Benzidine) prepared by mixing (1.84 g; 0.01mol) of benzidine dissolved in (10 mL) of absolute ethanol with (2.64 g; 0.02 mol) of cinnamaldehyde dissolved in (10 mL) of absolute ethanol, then three drops of glacial acetic acid were added to the prepared mixture and left under reflux for two hours, producing yellowish solid product.

The solid product formed was separated by filtration, purified by recrystallization from ethanol, washed with ethanol, and then dried

[11]. Azure A is an organic compound with the chemical formula $C_{14}H_{14}ClN_3S$. It is a light blue to dark blue dye. Azure B is an organic compound with the chemical formula $C_{15}H_{16}ClN_3S$. Composition is given in Figure (1- a, b).



(a)



(b)

Fig.1-a, b: 2D Structure of azure A and azure B organic dyes

Solutions of concentration ($1x10^{-3}$ M) for each of organic dyes and liquid crystalin ethanol solvent were prepared. The powder was weighed by using an electronic balance type (BL 210 S), Germany, having a sensitivity of four digits. Different concentrations were prepared according to the following equation [12]:

$$\mathbf{W = \frac{M_W \ x\ V\ x\ C}{1000}} \quad (10)$$

Where

W: weight of the dissolved in material (g)

M_W : Molecular weight of the material (g/mol)

V: Volume of the solvent (mL)

C: the concentration (mol/L)

The prepared solutions were diluted according to the following equation:

$\mathbf{C_1 V_1 = C2\, V_2}$ (11)

Where

C_1: primary concentration

C_2: new concentration

V_1: the volume before dilution

V_2: the volume after dilution

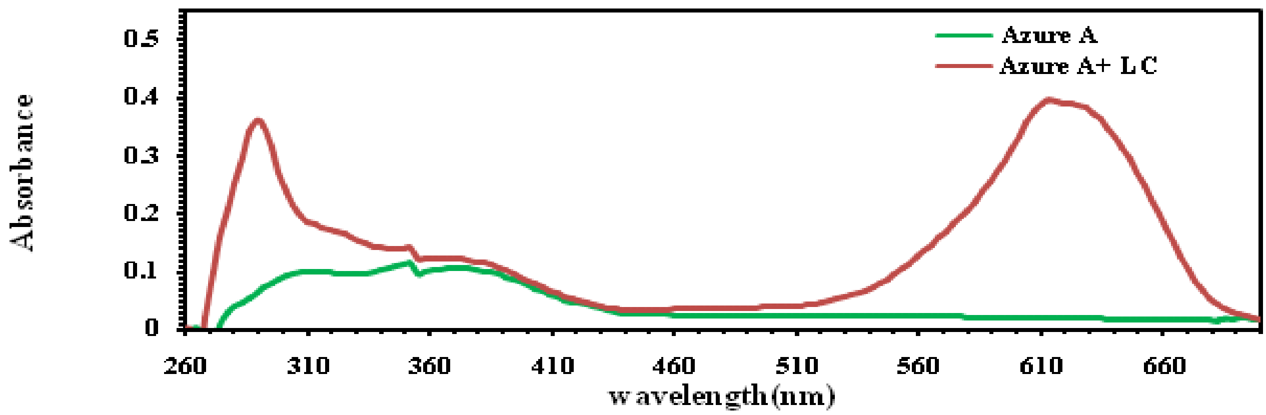
In this work, concentrations (1x10-4 M) were prepared for each of organic dyes and liquid crystals in ethanol solvent were prepared.
Then we mixed each organic dye with liquid crystal in ratio (5:5) mL by using the magnetic stirrer at room temperature.

Result and Discussion

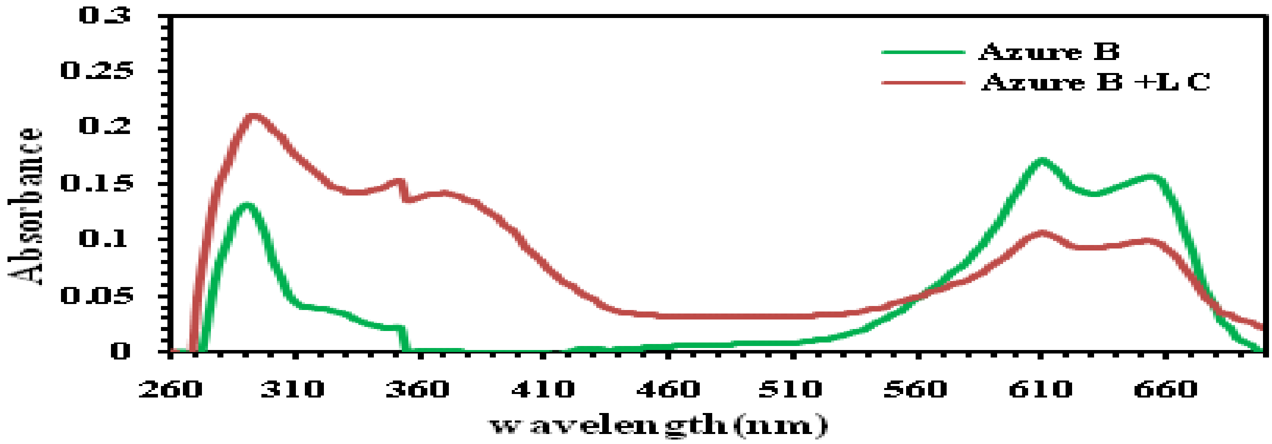
The linear optical properties and Z-Scan experiments will be explain in detail in the following paragraph:

Linear Optical Properties

The linear absorption and transmission spectra for each of organic dyes and liquid crystal in ethanol solvent at concentrations (1×10^{-4} M) recorded for wavelengths (190 to 1100) nm were tested using UV-VIS spectrophotometer model (Aquarius 7000, Optima ,Japan) , at room temperature, as shown in Fig. (2-a,b) respectively as solutions. The present results show that the absorption peaks for (azure A and azure B) as pure organic dyes in ethanol solvent were small with compared to the same samples doping with nanoparticles of liquid crystals materials due to increasing number of molecules per volume unit. The linear refractive coefficient (n_o) and linear absorption coefficient (α_o) obtained from equations (6 and 7) respectively, of pure and doping organic dyes (azure A and azure B), at concentration of (10^{-4} M).The values of (α_o) for doping organic dyes are larger those values for pure organic dyes, as listed in Table (1).



(a)



(b)

Fig.2-a, b: Absorption spectra for of (azure A, azure A + liquid crystal, azure B and azure B +liquid crystal) at concentration (10^{-4} M)

Z-Scan Measurements

The Z-Scan experiments were performed using a continuous wave (CW) diode solid state laser at (457 nm) wavelength and (56mW) power, which was focused by (15mm) focal length lens. Where the radius of laser spot was (0.0353 cm) and the incident laser intensity on the sample of (30.270kWatt / cm^2).The schematic of the experimental set up used is shown in Figure (3). A (1mm) wide optical cell containing the solution of each of (pure organic dyes in ethanol solvent and the same samples doping with nanoparticles of liquid crystals materials) is translated across the focal region along the axial direction that is the direction of the propagation laser beam. There are two methods of Z-Scan technique, closed aperture to obtain nonlinear refractive coefficient, and open aperture method to obtain nonlinear absorption coefficient. The far field intensity is measured as a function of the sample position by properly monitoring the transmittance change through a small aperture at the far field position (closed aperture) [13].The third-order nonlinear refractive coefficient n_2,and the nonlinear absorption coefficient, β, of all samples in ethanol solvent at different concentrations were evaluated by the measurements of Z-Scan.

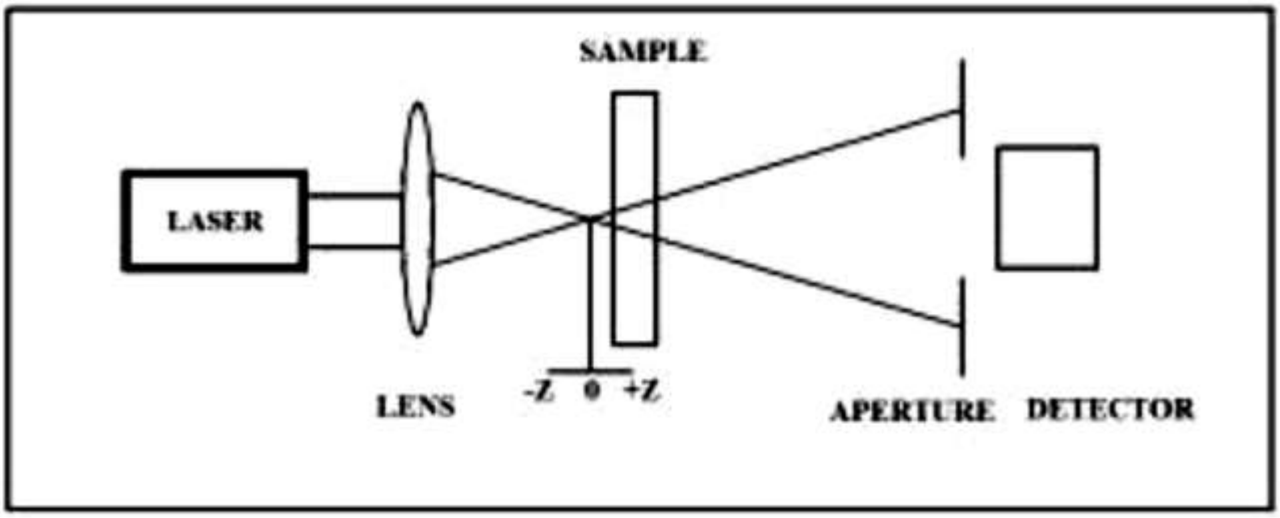


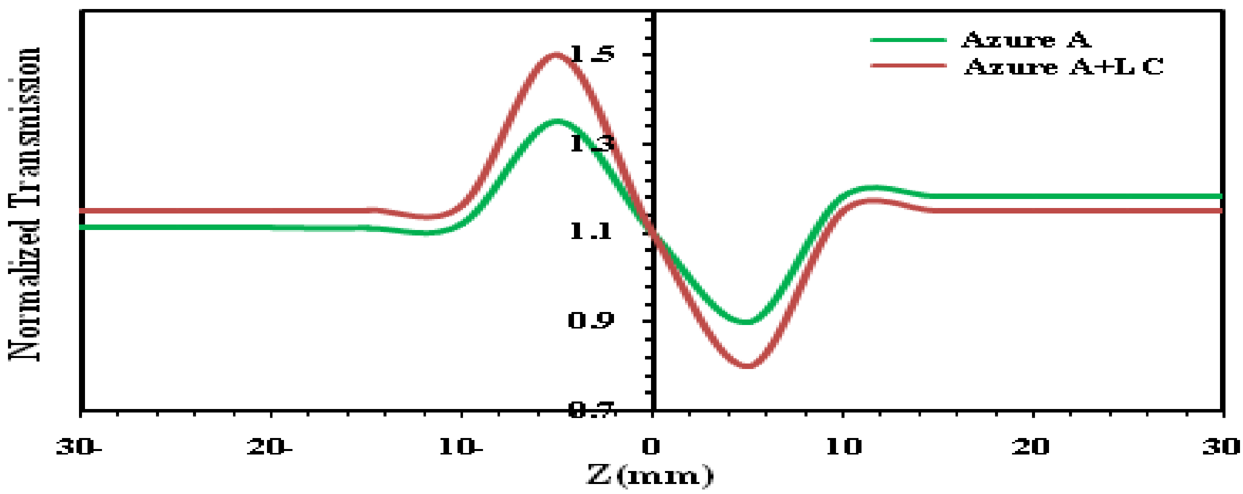
Fig.3: Schematic diagram of Z-Scan experimental arrangement

Nonlinear Optical Properties

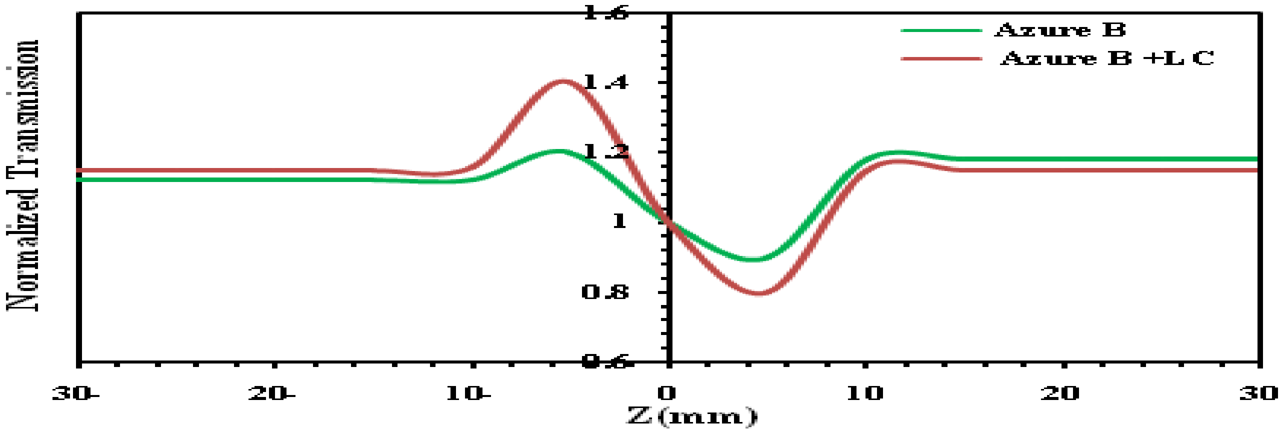
The nonlinear properties of(pure organic dyes in ethanol solvent and the same samples doping with nanoparticles of liquid crystals materials at concentration (1×10^{-4} M) in ethanol solvent, were measured by the Z-Scan technique. The nonlinear refractive coefficient (n_2) by closed-aperture Z-Scan measurements and nonlinear absorption coefficient (β) by open-aperture Z-Scan.

The measurements were done at 457nm, 56mW.Figures (4-a, b) shows closed-aperture Z-Scan of (azure A and azure B) organic dyes in ethanol solvent and the same samples doping with nanoparticles of liquid crystals. The nonlinear effect region is extended from (-3) mm to (3) mm. The peak followed by a valley transmittance curve obtained from the closed aperture Z-Scan data indicates that the sign of the refraction nonlinearity is negative ($n_2 < 0$), leading to self-defocusing lensing in the sample. To investigate the nonlinear absorption coefficient, Figures (5-a,b) shows open-aperture Z-Scan of (azure A and azure B)organic dyesin ethanol solvent and the same samples doping with nanoparticles of liquid crystals .Its noticed, also from these Figures (two photon absorption) phenomenon.

The nonlinear parameters are calculated, as tabulated in Tables (1) from this Table we show that the values of nonlinear parameters (n_2 and β) for organic dyes doping with liquid crystal are higher than as compared with pure organic dyes.

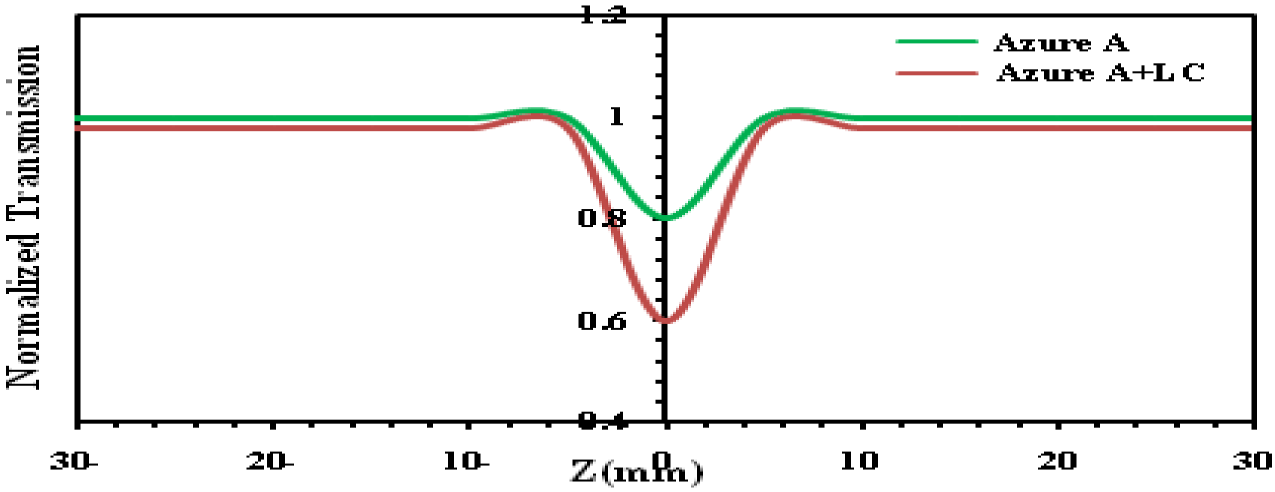


(a)

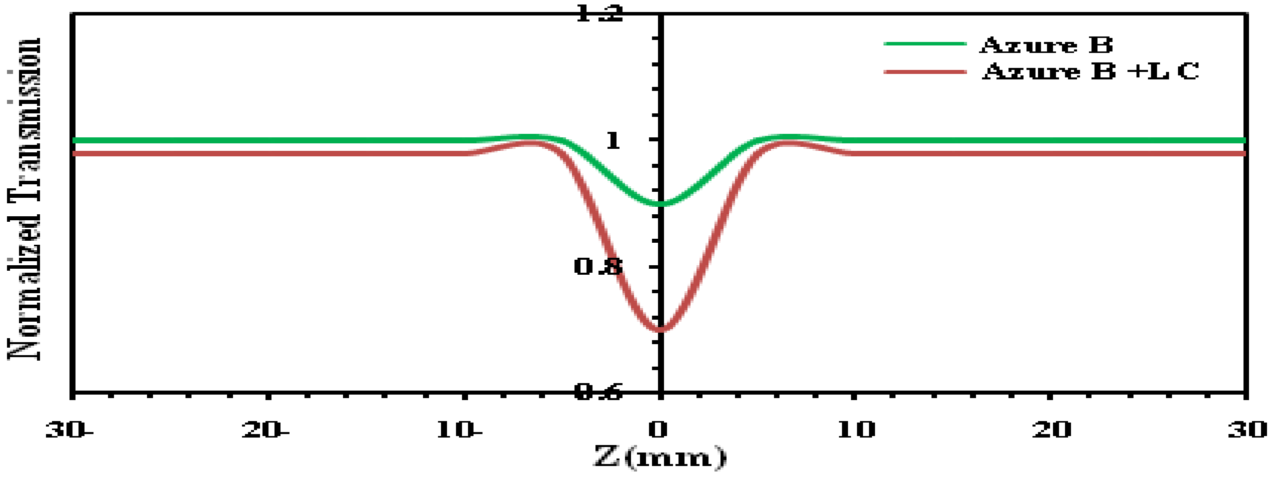


(b)

Fig.4-a, b: Closed-aperture Z-Scan data for (azure a, azure A +liquid crystal (LC), azure B and azure B +liquid crystal) at concentration (10^{-4} M)



(a)



(b)

Fig.5-a, b: Open-aperture Z-Scan for (azure A, azure A +liquid crystal (LC), azure B and azure B +liquid crystal) at concentration (10^{-4} M)

Table 1: The nonlinear optical parameters (azure A, azure A +liquid crystal (LC), azure B and azure B +liquid crystal (LC) at concentration (10^{-4} M)

Materials	T%	$\alpha_\circ$ cm^{-1}	$n_\circ$	ΔT_{p-v}	$\Delta\varphi_\circ$	$n_2\times10^{-11}$ cm^2/W	T(z)	$\beta\times10^{-3}$ cm/W
Azure A	0.9445	0.0571	1.4068	0.45	1.1083	2.2757	0.8620	0.7666
Azure A+LC	0.9234	0.0797	1.4986	0.70	1.7241	4.1544	0.8230	0.8070
Azure B	0.9885	0.0116	1.1646	0.35	0.7389	1.7264	0.7800	0.6508
AzureB+LC	0.9284	0.0743	1.4774	0.60	1.4778	3.5354	0.7028	0.7048

Conclusion

By using Gaussian beam from CW diode pump solid state laser at 457nm, we studied the nonlinear optical properties of several thiazine dyes such as (azure A and azure B) organic dyes doped with nanoparticles of liquid crystals nanoparticles materials in ethanol solvent at concentration10^{-4} M, by using Z-scan technique. The nonlinearity of doped organic dyes is larger than those for pure organic dyes. As well as all samples of azure a (pure or doped with liquid crystals) possess very large nonlinearity as compared with samples of azure B. The relation between the nonlinear refractive index and the nonlinear phase shift is a linear increasing relation. Z-Scan measurements indicated that all samples of pure and doped organic dyes exhibited negative nonlinear refractive index, and (Two Photon Absorption) behavior. So It is good materials for field of nonlinear optics (NLO) and its applications because of their large non-response nonlinearity and their extended spectral transparency, and can be available for applications as active laser medium.

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